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POLYVINYL ALCOHOL SYNTHETIC FIBER FOR CEMENT REINFORCEMENT USE
[Semento Hokyoyo Poribiniru Arukorukei Gosei Sen'i]

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TITLE 54 : POLYVINYL ALCOHOL SYNTHETIC
FIBER FOR CEMENT
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Poribiniru Arukorukei Gosei
Sen'i

SPECIFICATION

/361*

1. Title

Polyvinyl Alcohol Synthetic Fiber for Cement Reinforcement Use

2. Claims

1. Polyvinyl alcohol synthetic fiber for cement reinforcement use that is coated with 0.05 to 2.0 % by weight of polyvinyl alcohol having polar groups.

2. Polyvinyl alcohol synthetic fiber for cement reinforcement use stated in Claim 1, wherein the fiber is coated with 0.05 to 2.0 % by weight of an admixture solution containing 20 % by weight or higher of polar-group-free polyvinyl alcohol based on the polar-group-containing polyvinyl alcohol.

3. Polyvinyl alcohol synthetic fiber for cement reinforcement use stated in Claim 2, wherein the fiber is coated with 0.05 to 2.0 % by weight of an admixture solution that is comprised of the aforesaid admixture solution of the polar-group-containing polyvinyl alcohol and polar-group-free polyvinyl alcohol and of 20 % or more by weight of a fiber-treatment oil agent based on the total polyvinyl alcohols.

3. Detailed Description of the Invention

The present invention pertains to polyvinyl alcohol (hereinafter abbreviated as PVA) synthetic fiber for improving, in particular, bending strength of inorganic molding materials and building and

* Number in the margin indicates pagination in the foreign text.

structural components composed of various kinds of hydraulic cements, such as Portland cement, etc.

According to the present invention, PVA fiber is coated with a PVA having polar groups so as to form electrical and chemical affinity between the PVA fiber surface and the surface of cement particles or cement gel, thus achieving the initial-adsorption and permanent-adhesion effects of said PVA, and, without adversely affecting this electrical and chemical affinity and adhesion, the combined use of a fiber-treatment oil agent with the PVA further improves the dispersibility of the fiber in water or hydraulic matrices, such as cement, etc., and thus increases the fiber's contribution to bending strength. More specifically, the present invention uses a PVA having polar groups alone or mixes and uses it with a regular PVA that does not have polar groups and also with a fiber-treatment oil agent so as to modify the PVA fiber surface and to improve its adhesion and dispersibility, thereby providing PVA fiber that can prevent what is called a "slip-out" phenomenon, that is, a phenomenon in which fiber comes out from a hydraulic matrix, such as cement, etc., and that fully exerts its effects as a cement-reinforcing fiber with its mechanical properties.

Structures and formed products (hereinafter referred to as /362
formed products, etc.) of various types of cements, a typical example
of which is Portland cement, have been extensively used in the field
of construction and civil engineering owing to their excellent

compression strength, incombustibility, durability, and the like as well as their low cost. However, they have weak impact resistance and extremely poor bending strength and readily form cracks. To correct these shortcomings, there are (1) a method that uses steel frames and reinforcing steels, (2) a method that mixes inorganic fibers or organic fibers, and (3) a method that combines methods 1 and 2 for increasing the effects of these methods. The present invention pertains to methods 2 and 3. Although various proposals have been made with respect to methods 2 and 3, there is no satisfactory method at present. A typical example of inorganic-fiber reinforcement is seen in asbestos cement slates, etc., which use asbestos. However, it has been strongly pointed out in recent years that asbestos is toxic from the viewpoint of handling. In addition, most of the asbestos supply must be imported, and one hears about the depletion of world asbestos supplies and the resulting price increase. Accordingly, there is a demand for a material that can replace asbestos as an industrial material.

Reinforcement with the use of glass fibers has also been considered in various proposals. Glass fibers, however, corrode due to the strong alkalinity of cement slurry or mortar, and it is difficult for them to retain their strength for a long period of time. As disclosed in JP-A-S49-99311, the use of glass fiber, including ZrO_2 , to which is imparted alkali resistance has been proposed, but its deterioration in formed products over an extended period of time is

not negligible; thus, this method does not provide a satisfactory solution. In recent years, attempts have been made to reinforce cement with [illegible] fibers, but they do not adhere well to cement, and they present a further problem of deterioration by rusting.

Also proposed is the use of various types of organic fibers for reinforcement. The main objectives of reinforcing cement formed products, etc., with organic fibers are (a) improvement of impact resistance, (b) improvement of flexibility (bending strength), and (c) improvement of both (a) and (b). Characteristics that are essentially required of fibers in order to achieve the aforesaid objectives are appropriate ductility for absorbing impact in the case of achieving objective a, and, in the case of achieving objective b, a Young's modulus of elasticity and strength that are higher than those of cured cement products according to general reinforcement theories. In order to effectively utilize these characteristics, fibers must be uniformly dispersed in cement formed products, etc., and must have excellent adhesion to cement. Furthermore, the fiber properties should not deteriorate in cement formed products that exhibit strong alkalinity. In other words, having good alkali resistance over a long period of time is another absolutely essential requirement when the use condition of formed products is considered. None of various organic fibers that have been proposed thus far satisfies the aforesaid conditions, though they may, at best, achieve (a) improvement of impact strength. More specifically, polyolefin fibers, such as

polypropylene, polyethylene, etc., have low strength and a low Young's modulus of elasticity and also have low adhesion strength because they are hydrophobic; as a consequence, they do not contribute to the improvement of bending strength although they improve impact strength slightly because they have large ductility. The same can be said for polyamide fibers, such as Nylon 6, Nylon 66, etc., poly(vinyl chloride), poly(vinylidene chloride), and the like. Although polyester fibers have relatively high strength and a high Young's modulus of elasticity, the ester groups in the macromolecular chains that form these fibers are hydrolyzed with an alkali, and, as a matter of course, the Young's modulus of elasticity and strength deteriorate substantially. Therefore, it is a widely known fact that the application of these fibers to cement formed products, etc., exhibiting strong alkalinity has a fundamental problem. Furthermore, reclaimed fibers, such as rayon, etc., also have a shortcoming with respect to alkali resistance, and natural fibers, such as wool, cotton, etc., swell in an alkaline condition and also exhibit low strength and a low Young's modulus of elasticity.

Among general-purpose organic fibers, PVA synthetic fibers, which are said to have a high Young's modulus of elasticity, high strength, and high alkali resistance and also said to have relatively good adhesion with cement because they are relatively hydrophilic, improve (b) flexibility, and they can also improve impact resistance since they exhibit appropriate ductility; therefore, it is a widely known

fact that they are suitable as reinforcement material for cement formed products, etc., and a large number of patents have been applied for on this subject. For example, a method for preparing slates with the use of PVA fibers having high strength and low ductility has been proposed. However, when this and other methods proposed in disclosed patents were replicated, it was learned that the physical properties of PVA fibers were not fully utilized. More specifically speaking, the PVA fibers inside slates exhibited what is called a "slip out" phenomenon, that is, a phenomenon in which the fibers are pulled out from a hydraulic matrix, such as cement, etc., when a bending fracture takes place; thus, it was found that the adhesion of the fibers with cement, which is the matrix in cement formed products, was not satisfactory. /363

The present inventors researched extensively to prevent this "slip out" phenomenon and, as a result, learned that, when the surface of a PVA fiber was improved by applying only a PVA having polar groups, by mixing it with a regular polar-group-free PVA and applying the mixture, or by further adding a fiber treatment oil agent to the mixture and applying it, thus improving the adhesion and dispersibility of the PVA fiber, it becomes possible to fully utilize the PVA fiber's mechanical properties so as to achieve its effects as a cement-reinforcing fiber. Based on this finding, the present invention was achieved.

Generally speaking, according to the reinforcement mechanism, when a tensile force is applied to a composite material in which short fibers are evenly dispersed in a cement matrix and the fiber and matrix bend in one piece according to the Hooke's law, the average tensile stress σ_0 of this composite material is given by the following equation:

$$\sigma_0 = [E_f V_f \eta + E_m (1 - V_f)] \epsilon$$

wherein E_f and E_m are the modulus of elasticity of the fiber and that of the matrix; V_f is a volume fraction; ϵ is distortion; and η is the orientation coefficient of the fibers. Since the stress at the time of bending can be divided into a compression-side stress and pull-side stress, Equation 1 can be employed.

From this Equation 1, one can see that, when the modulus of elasticity of the fiber is higher and the volume fraction is higher, the tensile stress of the composite material becomes higher and effective. From an economical point of view, however, it is, of course, better to achieve a higher effect by adding fibers having a high modulus of elasticity at a low rate. If one further studies the effect, one finds that, in addition to the effect of the orientation coefficient of the fiber, the effect of the interfacial adhesion strength between the fiber and matrix is necessary. In other words, the reinforcing efficiency becomes an issue. As stated in the foregoing, perfect interfacial adhesion strength cannot be expected

from any organic synthetic fiber. For this reason, the idea of the minimum required length and limiting aspect ratio of the fibers surfaces. When a tensile force acts in the axial direction of the fibers and causes a fracture, the following relationship is present. When the fracture is determined by the ultimate shear adhesion strength τ_u ,

$$l_0/d = \sigma_f / 2\tau_u \quad (2)$$

and when it is determined by the ultimate axial directional stress σ_f [illegible],

$$l_0/d = \sigma_f[\text{illegible}] / 2\tau \quad (3)$$

Here, l_0 is the limiting length of the fiber; d is the diameter of the fiber; σ_f is the axial directional stress of the fiber; τ is the shear adhesion stress of the fiber and matrix.

In the aforesaid Equations 2 and 3, l_0/d (limiting aspect ratio) has a direct relationship with τ_u and σ_f [illegible], and the length l of the fibers must be $l \geq l_0$.

As seen in the foregoing, for fiber-reinforced cement concrete, it is expected that l_0/d must be large to make up for insufficient τ and τ_u if the "slip out" phenomenon of the fibers is to be prevented. Reducing d and increasing l_0 , that is to say, l , to increase l_0/d are not a problem, theoretically, but it presents problems in actual processing and operation. This amounts to decreasing the fiber size or increasing the fiber length. If the size of the fiber is below a

certain degree, this leads to problems in operation, and, even if l/d is increased, fiber balls, etc., will be formed, thus presenting problems with respect to dispersion. Thus, for achieving uniform dispersion, it is better for l to be as short as possible, but the fiber will not exhibit a reinforcing effect because of the limiting aspect ratio. Therefore, the present invention solved the problem of obtaining both the reinforcing effect and good dispersion, that is to say, increasing τ_u and τ , by treating the surface of PVA fiber.

As the method of improving the interfacial bonding strength between a fibrous reinforcing material and cement matrix, methods of, for example, coating fibers with vinyl emulsion resins are presented in JP-B-S43-19432, JP-B-S53-6168, etc. The adhesion of reinforcing fibers and hydraulic substances, such as cement, etc., not only involves physical adhesion strength but also initial adsorption and affinity to the fiber surface. By increasing these by means of an electrical interfacial phenomenon and chemical reaction between the reinforcing fibers and the cement particles and cement gel in a cement matrix, permanent adhesion is formed in the process of hydraulic solidification of the cement matrix, thus further strengthening the adhesion. In this manner, the present invention provides a novel PVA fiber with enhanced adhesion.

As the PVA fibers for use in the present invention, any of the following (1) through (6) may be used:

- (1) fibers prepared by wet-spinning a completely saponified PVA aqueous solution in a Glauber's salt and by drawing/heat-treating at a total draw ratio of 600 % or higher,
- (2) fibers obtained by acetalizing the fibers described in (1) under stretched and non-stretched conditions,
- (3) fibers having a draw ratio of 900 % or higher and a boric acid content of 0.1 to 0.7 % that are prepared by adding boric acid to a completely or partially saponified PVA and by spinning it in a caustic alkali Glauber's salt bath,
- (4) fibers obtained by acetalizing the fibers described in (3) under stretched and non-stretched conditions,
- (5) fibers having a total draw ratio of 800 % or higher that are prepared by dry-spinning a completely saponified PVA, and
- (6) fibers described in (1) through (5) that are in a filament-shape /364 or a tow-shape.

The surface treatment can be carried out by any of the following methods or the like:

- (1) a method according to which, in a wet-spinning process, filaments or tows that have been washed with water are subjected to an immersion treatment in a stretched condition and then undergo a drying process and drawing/heat-treatment process, followed by winding (an in-process, predrawing treatment method),
- (2) a method according to which, in a wet-spinning process, filaments or tows that have been washed with water and dried undergo a

drawing/heat-treatment and subsequently are subjected to an immersion treatment in a stretched condition and then dried, followed by winding (an in-process, post-heat-treatment treatment method),

(3) a method according to which filaments or tows that have been spun and wound to form a finished product are once again continuously washed with water and swollen in a stretched condition and introduced into a treatment tank for coating and then dried and wound (a posttreatment method), and

(4) a method according to which filaments or tows that have been spun and wound to form a finished product are cut to a given length, and the short fibers are treated by immersing them in a treatment solution and then dried (a post-cutting, posttreatment method).

However, the method that does not adversely affect the properties of the fibers and that yields good adhesion and dispersion is Method 1, the in-process, predrawing treatment method. According to this method, the swollen fibers are immersed in a treatment tank in a stretched condition and dried; therefore, the coating adheres well to the PVA fiber surface, and, because the fibers further undergo a drawing/heat-treatment process, adhesion among the pasted fibers is eliminated, thus improving dispersion and swelling in water. Thus, this is the best method. The (2) in-process, post-drawing treatment [sic] is the same as what is called a fiber-finish-treatment method. This method causes a slight deterioration in dispersion, but the properties of the fibers do not change, and the treatment is easily carried out. The (3)

posttreatment method has a problem in that fibers that have been wound once are treated and processed again. However, it is a suitable method for treating small quantities. The (4) post-cutting, posttreatment method is troublesome from the viewpoint of handling, and, because it is a non-stretched treatment, the Young's modulus of PVA fibers tends to decrease or ductility to increase, but it is suitable for a small-quantity treatment or batch processing.

The following explains the polar-group-containing PVA that is used for the surface treatment. First, as cationic PVAs, there are aminoacetalized PVAs obtained by a posttreatment of PVAs and those obtained by a reaction with a quaternary ammonium salt. As copolymers, polar-group-containing PVA copolymers can be obtained by polymerizing vinyl acetate monomers and copolymerizable monomers thereof and subsequently by saponifying the obtained copolymers. Here, the following monomers are used: nitrogen-containing cationic PVAs, such as N-allyl urethane, N-allyl acetamide, acrylonitrile, acrylamide, hydroxymethyl crotonamide, N-vinyl succinimide, N-vinyl phthalimide, 5-ethyl-2-vinyl pyridine, vinyl imidazole, vinyl pyrrolidone, allylamine, aminoalkyl acrylate, etc.

At the same time, PVAs having anionic polar groups are also useful, and chlorinated, sulfonated, etc., PVAs that are obtained by a posttreatment of PVAs can also be used. As copolymers, polar-group-containing PVA copolymers can be obtained by polymerizing vinyl acetate monomers and copolymerizable monomers thereof and subsequently

by saponifying the obtained copolymer. Here, the following monomers are used: maleic acid, itaconic acid, crotonic acid, acrylic acid, etc., and salts thereof, and these anionic PVAs are also effective.

PVAs that are obtained from commonly used vinyl acetate and whose degree of polymerization is 300 to 3000 and degree of saponification is 86 to 99.9 mol % can also be used in combination for the purpose of improving adhesion.

Furthermore, the aforesaid PVA resin for coating use may incorporate 0.1 to 5 % of boric acid in an acidic state. It is also possible to add inorganic salts and gelling agents that are also coagulants of common PVAs to an extent that no gelling takes place. Some examples are $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 , K_2SO_4 , ZnSO_4 , CuSO_4 , FeSO_4 , MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$, NH_4NO_3 , KNO_3 , $\text{Al}(\text{NO}_3)_5$, NaCl , KCl , Na_3PO_4 , K_2CrO_4 , etc.

These polar-group-containing PVAs or these in combination with regular PVAs polymerized from vinyl acetate are applied to PVA fibers, and, if the quantity of the PVA adhering to the PVA fibers increases, the affinity and adhesion between cement and fibers improve, but it also starts affecting the adhesion between fibers, thus deteriorating dispersion in cement slurry or water and making it difficult for the fibers to exert their effects. As a consequence, the bending strength of cement formed products, etc., does not improve. Accordingly, in order to maintain the adhesion between cement and fibers and also to improve dispersion without causing adhesion between fibers, the

present inventors found that a combined use of a polar-group-containing PVA or regular PVA with a fiber-treatment oil agent yields a synergistic effect in imparting bending strength to cement formed /365 products, etc.

The oil agent here may be any of various types of fiber-use posttreatment oil agents, and some suitable examples of cationic oil agents are amines, such as stearic acid amylethyl ethanol amine, trimethyl stearyl amine chloride, stearyl amine, behenic acid diethanol amine, etc., including quaternary ammonium salts thereof, as well as imidazoline-type cationic oil agents.

As nonionic oil agents, ether compounds obtained by the polyethylene oxide addition of 1, 2, or 3 molecules of a higher fatty acid, such as stearic acid, palmitic acid, lauric acid, etc., or ester compounds obtained by the polyethylene glycol addition can be used. Furthermore, polyethylene oxide adducts, such as nonylphenyl ether, octylphenyl ether, isoocetyl stearate, sorbitan monostearate, castor oil ether, etc., and pluronic-type hydrophilic polyethers, etc., may also be used.

Among anionic oil agents, cetyl sulfate salts' POE adducts, which are compounds of cetyl alcohols, are suitable.

With respect to the concentration of the treatment solution, in the case of using a polar PVA alone and mixing and using it with a regular PVA, 1 to 50 g/L is appropriate, and 1 g/L or less is not a sufficient adhering quantity, whereas 50 g/L or higher leads to

foaming, undesirable viscosity, etc., and thus is not desirable from the viewpoint of handling. In terms of adhesion rate to PVA fibers, 0.01 to 2 % by weight of the fibers is appropriate. If the applied quantity of the PVA is 0.01 % by weight or less, adhesion is not improved much. If it exceeds 2 % by weight or higher, adhesion between fibers takes place, thus hindering dispersion. It is preferably 0.05 to 0.5 % by weight. With respect to the mixing ratio of the polar-group-containing PVA and regular PVA, it is desirable to mix 20 % by weight or higher of the regular PVA with the polar-group-containing PVA. With this ratio, both the affinity and adhesion of the polar-group-containing PVA and regular PVA with cement are utilized, thus strengthening the adhesion effect.

The concentration of the fiber-treatment oil agent employed when it is added to the other components and used as a mixture is 1 to 30 g/L. If the concentration is 1g/L or less, the oil agent does not contribute to dispersibility, and a concentration exceeding 30 g/L leads to poor handling due to foaming, etc., and is also not economical. Since it is used in combination with the polar PVA and regular PVA, its adhering quantity to the fibers is 0.01 to 2 % by weight, preferably 0.05 to 0.5 % by weight. If the adhering quantity is less than 0.01 % by weight, the oil agent does not contribute much to adhesion and dispersibility, and 2 % by weight or more leads to poor handling due to foaming, etc., and is also not economical.

The suitable addition rate of this fiber-treatment oil to the polar PVA or a mixture of the polar PVA and regular PVA is 20 % by weight or more based on the total PVAs. An addition rate of 20 % by weight or less is not sufficient, and the dispersion effect of the oil agent is small.

Explaining three kinds of fibers used in the present invention, that is, fibers having a polar-group-containing PVA, fibers having a mixture of polar-group-containing and polar-group-free PVAs, and the preceding fibers to which a fiber-treatment oil agent is further added, firstly, electrical and chemical factors owing to the polar groups contained in the PVA molecular chains; cement particles and cement gel products, such as tricalcium silicate, dicalcium silicate, tricalcium aluminate, tetracalcium aluminate, etc., which are structural compounds in the cement hardening process; adsorption of cement particles and gel by the PVA-fiber-coating PVA and oil agent owing to electrical cohesion and repulsion as well as chemical affinity; and cohesion and dispersion within cement particles and gel contribute to the improvement of initial adhesion strength. Secondly, the PVA fibers that are surface treated and the cement solidified product are adhered at their interface, thus forming adhesion with high polymer strength and improving permanent adhesion. Thirdly, dispersibility is improved when certain polar PVA treated PVA fibers are dispersed in a cement slurry or water. This is believed to be based on the theory that swelling takes place owing to the PVA on the surface of the PVA fibers

and the oil agent, and these have a hemicellulose-like dispersing function, as Kozo and Mitsumata used in Japanese paper.

Filaments and tows obtained by methods other than the post-cutting treatment method are cut into a 2 to 25 mm length, preferably a 3 to 15 mm length, and dispersed in cement mortar, concrete, etc., thus using them alone, or they can be used in combination with asbestos fibers, alkali-resistant glass fibers, plant fibers, such as pulp, etc., or organic synthetic fibers. Furthermore, in the form of cement mortar, cement concrete, or aggregate in which the reinforcing PVA fibers are used, sand or gravel may be mixed and used together /366 with these, or they may be used together with reinforcing steel or steel frames.

The fibers of the present invention can be utilized for pressure molding, vibration molding, pressure-vibration combination molding, centrifugal molding, paper-making [as transliterated] molding, wind-up [as transliterated] molding, vacuum molding, and extrusion molding.

The fibers of the present invention in filament form are used for filament winding, molded products in sheet forms, molded products in thick sheet forms, reinforcing-steel-containing molded products, etc., that will be utilized for products that receive stress in the axial direction of the fibers. In the forms of woven cloth, net, or nonwoven cloth, they can be used for molded products in sheet forms and cylindrical molded products. The scope of applications of the PVA fibers of the present invention encompasses any area in which these

fibers can be utilized fully as the reinforcing material of solidified cement, plaster, etc., and some examples include structural materials, such as cement roof tiles, thick slates, corrugated asbestos slates, asbestos cement boards and secondary products thereof, asbestos perlite boards, asbestos cement pipes for city-water use, pulp cement pipes, asbestos cement cylinders, excelsior and cement chip boards, concrete boards, concrete blocks, cast stones, mortar boards, terrazzo blocks, terrazzo tiles, reinforced concrete assembled walls, concrete prefab components, prestressed concrete double T slag, etc., planks or reinforced concrete planks, prestressed concrete planks, centrifugal reinforced concrete foundation piles, reinforced concrete pipes, centrifugal reinforced concrete pipes, centrifugal reinforced concrete balls, etc. Not limited to the aforesaid cement products, the present invention can be used for other structural materials, interior materials, and construction materials, and no limitation is imposed when these materials are used.

The following explains the present invention, referring to working examples and comparative examples.

Working Example 1 and Comparative 1

A PVA whose polymerization degree was 1730 and saponification degree was 99.9 mol % was formed in a 16 % aqueous solution, and boric acid in a quantity of 2 % was added to this stock solution. The solution was spun into a caustic alkali Glauber's salt aqueous solution through a metal plate having 1000 holes. After the spun yarns

were neutralized and washed with water, they were dried and then drawn and heat-treated with a total draw ratio of 14.

The obtained fiber's unifilar denier was 1.8 dr, its postdrying strength was 98 kg/mm², its ductility was 5.3 %, the initial modulus of elasticity at that time was 3.4×10^3 kg/mm², and the residual boric acid was 0.3 %.

First, according to the following methods, some samples were prepared by treating this fiber during the production process and after winding and some by cutting and then treating.

(a) Filaments that had been wound were swollen in warm water, immersed in a treatment tank in a stretched condition, treated continuously in a 105° C hot-air drier, and wound. The filaments thus prepared were

cut into a 6 mm length and used as a sample (a posttreatment method).

(b) Filaments that had been wound were firstly cut into a 6 mm length and dispersed and swollen in water, immersed in a treatment solution, dewatered, and subsequently dried with hot air, thus obtaining cotton-like fibers, which were used as a sample (a post-cutting treatment method).

(c) During the fiber-production process, the fiber was immersed in a treatment tank in a stretched condition after it was washed with water, and a conventional method was carried out from the drying process on. The wound fiber thus prepared was cut into a 6 mm length and used as a sample (an in-process, predrawing treatment method).

(d) During the fiber-production process, the fiber was immersed in a treatment tank after a drawing/heat-treatment and then dried and wound, after which it was cut into a 6 mm length and used as a sample.

The following were used as the PVAs employed for the coating treatment.

(1) A 20 g/L aqueous solution of itaconic-acid-modified PVA (polymerization degree: 1700, saponification degree: 99.3 mol %, and degree of modification by itaconic acid: 1.3 mol %.)

(2) A 1:1 mixture of itaconic-acid-modified PVA and partially saponified PVA having a polymerization degree of 1740 and saponification degree of 96.5 % was formed into an aqueous solution containing said mixture at a concentration of 20 g/L.

(3) To the aqueous solution described in (2) was added 10 g/L of a fiber-treatment oil agent, a nonylphenyl ether POE adduct, thus obtaining a dispersion.

A comparative example was a sample with no coating treatment.

Evaluation of adhesion improvement

1. Bending strength test with premix board: Using ordinary Portland cement, the W/C was set to 0.5, and the sample fibers of (a) through (d) were mixed into the cement in a quantity of 2 % by weight of the cement, which was then poured into a mold form and press-formed and subsequently cured for 4 weeks in 20° C water. The bending strength of this product was tested.

2. Dispersibility test: The quantity of the fibers of (a) through (d) was set to 1.5 % of water, and, using a TAPPI standard disaggregation /36 machine, paper-making was carried out for 500 counts, and the dispersibility was evaluated by visual observation.

◎ Excellent: Each individual fiber was uniformly dispersed.

○ Good: Fibers were dispersed, but there was slight adhesion between fibers.

△ Normal

✗ Poor: Dispersibility was poor, and many fibers adhered together.

✗✗ Extremely poor: Fiber balls were formed.

3. Adhesion strength: In a cement having a W/C of 0.5, the fibers of (a) through (d) were buried at 5 to 10 mm below the surface. After the cement was cured for a given time, the fibers were pulled. The ratio of the number of fibers pulled out to the total number of the buried fibers was found, this ratio being taken as the adhesion strength. The results are shown in Table 1. Table 1 also shows the adhering quantity of PVAs.

TABLE 1

(g)	(h)	処理法と分量比 (%/PVA繊維)	(i)	(l)	(m)	(n)
	処理方法 (a)~(d)	1)イタコニ酸 PVA 2)イタコニ酸PVA +部分セイ化PVA 3)イタコニ酸PVA +油剤	(%)	分子量 (×10 ⁴)	引張強度 (kg/cm ²)	引張強度 (kg/cm ²)
1	(a)後処理方法	0.14			△ 192	0
2	(b)アフト横張り方法	0.18			× 180	0
3	(c)延伸横張り方法	0.11			○ 225	0
4	(d)延伸後横張り方法	0.15			△ 218	0
5	(e)		0.21		△ 200	0
6	(f)		0.29		× 190	0
7	(g)		0.10		○ 230	0
8	(h)		0.28		△ 220	0
9	(i)			6.23	○ 220	0
10	(j)			0.29	○ 218	0
11	(k)			0.11	● 255	0
12	(l)			0.21	◆ 220	0
13		(注)工場中何も無事しない			△ 150	1.0
14		(i)			△ 152	9
15		無事なし (k)延伸横張りで本物事			△ 143	1.2
16		(注)後処理方法で本に異常			- 80	-
17		アスベスト 6D 2% (k)			- 120	-

Key: a) posttreatment method; b) postcutting treatment method; c) predrawing treatment method; d) postdrawing treatment method; e) working example; f) comparative example, g) test No.; h) treatment methods; i) no treatment, (1) no coating during the process, (2) fiber was coated with water according to the predrawing method, (3) fiber was immersed in water according to the posttreatment method; j) plain; k) Asbestos 6D 2%; l) dispersibility; m) bending strength; n) adhesion (pulled ratio); o) treatment solution and adhering quantity (%/PVA fiber); (1) itaconic acid PVA; (2) itaconic acid PVA + partially saponified PVA; (3) (2)+ oil agent.

Compared with plain cement mortar shown in the comparative example, untreated PVA fibers, asbestos, etc., contributed to bending strength, and Test Nos. 2 and 6 of Working Example 1 had poor

dispersibility. However, Test No. 11 had good dispersibility as well as improved adhesion, and its bending strength was 1.7 times that of the untreated samples. The fiber-treatment timing also played an important role for achieving the coating effect.

Working Example 2

An aqueous solution of a PVA having a polymerization degree of 1760 and saponification degree of 99.8 mol % to which 3.8 % of boric acid was added was spun in a caustic alkali Glauber's salt bath using a metal plate having 1000 holes. In a sulfuric-acid acidic bath, the adhering caustic soda alkali was completely neutralized, and the filaments were washed with water to eliminate Glauber's salt and boric acid and [illegible] so as to set the boric acid content to 0.2 %. After [illegible], these filaments were divided into those that would and would not be immersed in a treatment tank and dried by a hot-air drier, followed by a drawing/heat-treatment and winding. The total draw rate was 14.5, and the residual boric acid content in the filaments was 0.2 %. The size of a single fiber was 2.0 dr. The strength of this fiber was 1.2×10^2 kg/mm², and its ductility was 5.2 %. Its Young's modulus was 3.5×10^5 kg/mm².

The treatment solutions used for the PVA surface treatment was prepared as follows:

(1) To an aqueous solution of a PVA whose polymerization degree was 1700 and saponification degree was 99.9 mol % was added, in a sulfuric-acid acidic condition, β -aminobutyl aldehyde dimethylacetal

to aminoacetalize it, thereby obtaining a basic polyvinyl alcohol. The degree of aminoacetalization was 2 mol %. This aminoacetalized PVA was formed into an 8 g/L aqueous solution.

(2) To the solution prepared in (1) was added a regular PVA whose polymerization degree was 1730 and saponification degree was 97.5 % at a mixing ratio of 3:7, and an aqueous solution having a total PVA concentration of 8 g/L was prepared.

(3) To the mixture solution prepared in (2) was added a fiber-treatment oil agent, a polyethylene oxide adduct of quaternary stearylamine, so as to set its concentration to 4 g/L, thereby obtaining a dispersion.

The coating of PVA fibers with the treatment solutions (1) through (3) was carried out according to two methods: (a) coating prior to drawing and (b) coating after winding. In Comparative Example 2 were presented fibers that were prepared under the same conditions as in Working Example 2 but that were not treated at all and that were treated only with water.

Evaluation of adhesion improvement

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1. Bending strength test of slates prepared by a paper-making method

1. The treated fibers were cut into 6 mm lengths, and 2 parts by weight of the cut fibers, 5 parts by weight of chrysotile asbestos 5R, a small quantity of pulp, and the remaining 93 parts by weight of ordinary Portland cement were formed into a water dispersion, which was subjected to a paper-making

process with a small-scale tester, thus forming a slate.

After a two-week air-exposure curing, the slate was tested for bending strength.

2. Dispersibility test: According to the same method described for Working Example 1.

3. Adhesion strength: The same as above.

The results are shown in Table 2.

TABLE 2

(c)	(f)	処理液と付着量(%) / PVA量(%) (j)			(k)	(l)	(m)
		水	PVA + 水	水 + PVA			
18	(a) 純水処理方法	0.68			○	320	0
19	(b) 純水処理方法	0.89			×	312	0
20	(a)		0.13		△	363	0
21	(b)		0.13		×	322	0
(d)	22 (a)			0.15	○	387	0
	23 (b)			0.15	○	365	0
	24 純水処理量(g)				△	282	13
	25 (a) 水のみで処理 (h)				△	279	18
	26 (a)				△	285	5
(e)	27 PVA 量(g) (i)				○	242	-

Key: a) predrawing treatment method; b) posttreatment method; c) test No.; d) working example; e) comparative example; f) treatment methods; g) fiber with no treatment; h) (a) that was treated only with water; i) PVA no [illegible]; j) treatment solution and adhering quantity (%/PVA fiber); k) dispersibility; l) bending strength; m) adhesion (pulled rate); (1) acrylamide modified PVA; (2) acrylamide modified PVA + partially saponified PVA, (3) (2) + oil agent.

As seen in the foregoing, by surface treating fibers with cationized PVA and further by improving dispersibility with a fiber-treatment oil agent, a strength improvement of about 40 % could be

achieved; as a consequence, modified PVA fibers having a high reinforcement efficiency that did not slip out in pull tests were obtained.